DRAFT 10/27/99

Lompoc Pesticide Air Monitoring
Fumigant Sampling and Analysis Plan

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Background

In 1997, the Department of Pesticide Regulation (DPR) formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns (first voiced in 1992) about pesticide use as it relates to community health. DPR has sought answers to whether health symptoms in Lompoc (Santa Barbara County) are occurring at a high rate and if so, to determine whether pesticides may be the cause.

The LIWG is composed of staff from federal, state, and county agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air monitoring strategy, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the Technical Advisory Group) developed a work plan that recommended comprehensive air monitoring in Lompoc during the growing season to determine whether applied pesticides migrate by air to adjacent residential areas. This exposure subgroup prioritized 46 pesticides based on their toxicity, use, and volatility.

The Technical Advisory Group (TAG) recommended a comprehensive monitoring program to span the peak use periods for the top 23 chemicals in a two-phase program. The TAG did not recommend monitoring for the remaining 23 pesticides from the original list of 46, realizing fiscal resources were limited. The first phase of monitoring was recommended for the summer of 1998 (if only partial funding was available), and the second phase for early summer of 1999 (Appendix A). The monitoring recommendation was designed to measure maximum daily pesticide concentrations in air that could be compared to human health endpoints. The LIWG accepted the TAG recommendations and forwarded them to DPR in April 1998.

In August 1998, the Legislature passed Senate Bill 661, which provided funding to DPR to conduct the first phase of pesticide air monitoring. The first phase of monitoring was completed in September 1998 (results are summarized in Section 3.2). In May 1999, DPR received a grant from the U.S. Environmental Protection Agency to monitor fumigant applications in the Lompoc area during fall and winter months. This document describes the monitoring planned for fumigants during the months of November 1999 through January 2000.

1.2 Data Quality Objectives for Fumigant Monitoring

1.2.1 *State the Problem*

Develop a Concise Description of the Problem - The problem is to determine if air concentrations of pesticides in Lompoc, California, exceed human health screening levels. Screening levels have been proposed by DPR in the absence of human health standards (Appendix B). Human health standards are typically generated by the U.S. Environmental Protection Agency or by California's Office of Environmental Health Hazard Assessment. Lompoc residents have voiced concerns about pesticide use as it relates to community health. An evaluation of available health-related data, including hospital discharges and cancer incidence, suggest that certain respiratory illnesses, such as asthma, bronchitis, and lung and bronchus cancers, occur in Lompoc at higher rates than in other comparison areas.

Identify Primary Decision-Maker - As the lead agency for the registration and use of pesticides in California, the DPR is the primary decision-maker for this project.

Identify the Members of the Planning Team - DPR formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns. The LIWG is composed of staff from federal, state, and county agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air monitoring strategy, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the Technical Advisory Group) assists in the planning, implementation, and evaluation of pesticide air monitoring in Lompoc. Members of the Technical Advisory Group (TAG) are listed in Appendix C.

Specify Available Resources and Relevant Deadlines - This project is being conducted in phases due to complexity and funding constraints. This phase of the project focuses on monitoring for fumigants used in the Lompoc area. This phase of the project is being conducted under a grant from the U.S. Environmental Protection Agency (Agreement E-999332-01-5). DPR will use the $100,000 in grant funds to contract for field sampling, laboratory analysis. Members of the TAG provide in-kind contributions, such as project planning and supervision, compilation of pesticide use data, compilation of meteorological data, evaluation of data, and report preparation. Field sampling and laboratory analysis for this phase will occur during a high use period for fumigants during the fall of 1999 and into the winter of 2000.

1.2.2 *Identify the Decision*

Identify the Principal Study Questions - Do air concentrations of fumigants used in the Lompoc area exceed the acute (24-hour) human health screening level? (This objective was reiterated during the TAG meeting on October 26, 1999. The concern of members who voiced an opinion was not over sub-chronic or chronic levels.) The fumigants to be monitored, if applied during the months of November, December, and January, include 1,3-dichloropropene, chloropicrin, metam sodium, and methyl bromide. (See section 1.2.4 for discussion of fumigant selection.) Extension of monitoring into April is currently under discussion with TAG members and the laboratory and field contractors.

Define Alternative Actions-

(a) no action is taken (Table 1).
(b) a more refined analysis is undertaken (Table 1).
(c) regulatory action is taken to reduce fumigant air concentrations (Table 1).

Combine the Principal Study Question and Alternative Actions into a Decision Statement -Determine if fumigant air concentrations are above screening levels and require regulatory actions to mitigate them.

1.2.3 *Identify Inputs to the Decision*

Identify the Information Required to Resolve the Decision Statement - There are two primary inputs required to resolve the decision statement, namely, air concentrations of fumigants in Lompoc and screening levels for those fumigants. Air concentrations of fumigants in the Lompoc area will be measured directly in this study to generate the data needed to compare with the screening levels. Acute (24-hour) screening levels have been proposed by DPR toxicologists for each fumigant to be monitored (Appendix B, Table 1). Other information may be useful or essential for interpreting pesticide air concentrations, such as sub-chronic and chronic screening levels, meteorological data, and pesticide use records. While there is likely to be pesticide exposure from routes other than air, inhalation exposure for fumigants is of primary concern due to the high volatility of fumigants and documented respiratory illnesses in Lompoc.

Determine the Sources for Each Item of Information - Information on fumigant air concentrations will be obtained by direct measurement during a high use period (November through January, Tables 2-4). Monitoring stations will be established in Lompoc to measure fumigant air concentrations during specific fumigant applications. Information on pesticide use will be obtained from pesticide use reports submitted by pesticide users to the Santa Barbara County Agricultural Commissioner's Office. Meteorological conditions will be measured by the Santa Barbara County Air Pollution Control District at its existing station in Lompoc. In addition, a MetOne station will be established in the agricultural area west of Lompoc and operated by staff from the DPR.

Confirm that the Appropriate Measurement Methods Exist to Provide the Necessary Data -The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith 1988). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel 1995; Keith 1988; Baker, et al. 1996). Chemical extraction methods for removing fumigants from sorbent media and analyzing with a gas chromatograph provide quantitation of air concentrations below the acute screening levels and associated decision rules (Table 5).

In addition, canisters have been used as an alternative to solid sorbents for air sampling (Keith 1988). However, at this time chemical analytical methods are only available for two of the four fumigants (1,3-dichloropropene and methyl bromide) using canisters as the air sampling method.

1.2.4 *Define the Study Boundaries*

Specify the Characteristics that Define the Population of Interest - The population of interest is the fumigants used in the Lompoc area. Based on pesticide use reports between 1996 and 1998, one fumigant, metam sodium, is used most in the Lompoc area during November, December, and January (Tables 2 - 4). Other fumigants may be used in the Lompoc area, such as 1,3-dichloropropene, aluminum phosphide, chloropicrin, methyl bromide, and sulfuryl fluoride. Very little aluminum phosphide is used in the Lompoc area (approximately six pounds per year). Therefore, exposure should be low, so it will not be monitored at this time. Sulfuryl fluoride is used for structural fumigations and its use is reported only on a countywide basis. The specific use pattern in the Lompoc area is currently under investigation by the County Agriculture Commissioner's staff. Therefore the TAG decided to defer consideration for monitoring of sulfuryl fluoride to a later date. No other fumigants were reported for the Lompoc area between 1996 and 1998 (DPR 1996, 1997a, 1998). Therefore, fumigant monitoring will include 1,3-dichloropropene, chloropicrin, methyl isothiocyanate (MITC, the biologically-active breakdown product of metam sodium, see section 5.1), and methyl bromide.

Define the Spatial Boundary of the Decision Statement – The spatial boundary of the decision statement is the outdoor air within the Lompoc city limit. The city of Lompoc, 10.9 square miles in area, is located in a coastal valley of Santa Barbara County, California, approximately eight miles east of the coastline (Figure 1). The valley is oriented roughly northwest to southeast. Between the city and the ocean lies an agricultural region predominantly devoted to vegetable and flower production. Predominant wind patterns during winter months tend to be north-west or westerly, moving across the agricultural region and into the city of Lompoc (Johnson, 1998, Figures 2 and 3).

For the purposes of this study, the boundary of the pesticide-use area is 38.8 square miles (Figure 3) and consists of the Township-Range sections listed in Table 6. This list of sections was previously accepted by the LIWG as reasonable for defining the area of pesticide use that could potentially affect air in the city of Lompoc.

Air monitoring will be conducted inside the city limits of Lompoc. Three of the five air sampling sites were selected to be representative of areas where the highest fumigant concentrations are hypothesized, based on proximity to fumigant application sites and predominant wind patterns during that time of year. The fourth site, near the center of Lompoc, was selected to be representative of fumigant concentrations that might be found closer to the center of the city. The fifth side is located in the north-east region of Lompoc to capture applications that might occur in the smaller agricultural areas to the north and east of the city.

Define the Temporal Boundary of the Decision Statement – In this project we will monitor fumigants during the expected high use period of fall and winter, based on pesticide use reports from 1996, 1997, and 1998 (DPR 1996, 1997a, and 1998). Specifically, fumigant applications will be targeted for monitoring during this period. The Santa Barbara County Agriculture Commissioner’s Office will notify field-sampling personnel via pager, approximately 24-hours prior to every fumigant application. Field staff will immediately notify DPR by pager, who will in turn immediately notify the primary laboratory by pager. Air monitoring will begin within 24 hours of notification of field sampling personnel in order to capture the time that applications are scheduled to begin. For safety reasons, air sample changes will not be conducted at night because samplers are located on roofs and are accessed with ladders. These roofs have no safety rails. Therefore air sampling will be conducted for 8 hours during daylight (+/- one hour) and 16 hours at nighttime (+/- one hour).

Scale of Decision Making - Decisions will be based on air concentrations measured at the monitoring sites established in the City of Lompoc.

Identify Practical Constraints on Data Collection - There are several constraints on data collection:

1. The time of monitoring is constrained to a specific, relativel high use season, namely November through January, for these four fumigants (Table 4). Each fumigant will be monitored individually (not simultaneously for all four fumigants) due to limited supply of air sampling equipment (owned by DPR). (Note: fumigants are analyzed separately due to different requirements for air sampling tubes, flow rates, and analytical methods.) Therefore, if fumigations occur for more than one fumigant at any given time, only one fumigant can be measured. The first fumigant to be applied will be monitored, unless monitoring has been completed for all planned fumigation events.

2. Sampling during high use periods does not necessarily ensure that maximum concentrations will be measured since air concentrations are dependent on factors other than use, including meteorological conditions and location of applications relative to air samplers.

3. Siting criteria for air sampler locations might prevent monitoring at locations of actual maximum concentration. The location of monitoring is constrained to the Lompoc area and places within that which meet the U.S. EPA siting criteria (Appendix D). Therefore, sites not meeting these criteria may have higher concentrations.

4. Due to monetary constraints, monitoring cannot be conducted on each day of the high use season, therefore days not monitored might have higher or lower concentrations.

5. Concentrations will be measured as 8- and 16-hour averages. Some chemicals can cause effects during shorter duration exposures.

6. The amount of monitoring is limited by the available funds.

7. Due to monetary constraints, this study will only provide information on pesticide active ingredients except in the case of metam sodium, where only the primary breakdown product will be analyzed (see section 5.1). Also, data will not be gathered for inert ingredients, adjuvants, industrial chemicals, or other pesticide product components that could potentially affect human health.

8. Methyl bromide may have non-agricultural uses in the area (e.g. structural fumigations of residences) and may be produced from natural sources (e.g. the ocean). There will be insufficient information to determine the relative contributions of each source to the overall air concentrations measured.

9. This study will only estimate inhalation exposure. Community exposure to pesticides by ingestion, dermal absorption, or other potential routes will not be measured.

10. There is insufficient toxicological information to determine the possible health hazard from exposure to multiple chemicals.

11. There is no evidence to indicate a problem from a dose below the no-observed-effect level (NOEL).

12. Some concentrations may be too low to quantify given the current state of our technology for chemical analysis.

13. Three monitoring sites are located on the western edge of Lompoc in an effort to measure maximum concentrations. This placement does not guarantee that higher concentrations won't actually occur at other locations. Based on our knowledge of wind patterns and the location of agriculture relative to Lompoc, this was deemed the logical place to focus our sampling efforts.
(Note: The placement of samplers was discussed with and agreed to by members of the

TAG in the March 1999. In that meeting it was decided to use four sites, three on the west side and one closer to the center of Lompoc. Subsequently, the LIWG approved the plan (Appendix E). In October 1999, the issue of number of sites was re-visited by the TAG with agreement on October 26, 1999 to add the fifth site in the north-east region of Lompoc.)

1.2.5 Develop a Decision Rule

Specify the Statistical Parameter that Characterizes the Population – For evaluating acute exposure to ambient air levels of individual fumigants monitored in this study, the parameter of interest will be the maximum 24-hour air concentration (averaged from sequential 8- and 16-hour concentrations) at any site or fumigation.

Specify the Action Level for the Study – For the purposes of this study, the action levels will be the screening levels. Screening levels for acute exposures have been proposed by the DPR (Appendix B).

Develop a Decision Rule – If the maximum air concentration is an order of magnitude below the screening level, no action will be taken (Table 1). If the maximum air concentration is between the screening level and an order of magnitude below the screening level, a more refined analysis will be undertaken (Table 1). If the maximum air concentration exceeds the screening level, DPR will explore the need for interim regulatory actions (Table 1). Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

1.2.6 Specify Limits on Decision Errors

Range of Concentration - Based on previous pesticide air monitoring in Lompoc and monitoring data from other studies, the possible range of concentrations for the fumigants is no detectable amount to 1000 micrograms per cubic meter (ug/m^3).

Identify the decision errors and choose the null hypothesis

Define Both Types of Decision Errors and Establish the True State of Nature for Each Decision Error – There are two decision errors, i) deciding that the maximum air concentration exceeds the screening level when it does not, and ii) deciding that the maximum air concentration does not exceed the screening level when it does.

> The true state of nature for decision error (i) is that the 99.9th percentile air concentration does not exceed the screening level.
> The true state of nature for decision error (ii) is that the maximum air concentration exceeds the screening level.

Specify and Evaluate the Potential Consequences of Each Decision Error - (i) If there is no health hazard, but inadequate or incorrect data indicate that there is a health hazard, DPR would mitigate the exposure without sufficient cause, with implications regarding pest management, alternative pesticides, crop yields, and costs to growers and consumers. (ii) If there actually is a health hazard, but inadequate or incorrect data indicate that there is no health hazard, public exposure could exceed levels considered safe. This may or may not result in adverse effects.

Establish Which Decision Error has More Severe Consequences Near the Action Level - Decision error (ii) has the more severe consequences because an unmitigated health hazard outweighs the consequences of economic costs.

Define the Null Hypothesis (Baseline Condition) and the Alternative Hypothesis and Assign the Terms False Positive and False Negative to the Appropriate Decision Error - The baseline condition or null hypothesis is that the maximum air concentration exceeds the screening level. The alternative hypothesis is that the maximum air concentration is below the screening level.

.

Specify a Range of Possible Values of the Parameter of Interest Where the Consequences of Decision are Relatively Minor (Gray Area) - The gray area is the region between the acute screening level and one order of magnitude below the screening level.

Assign Probability Limits to the Points Above and Below the Gray Region that Reflects the Tolerable Probability for the Occurrence of Decision Errors –
The following limits are proposed (Figure 4). Above the gray area: the tolerable probability of decision error is 5% between 66 and 100 $\mu g/m^3$ (for MITC); above 100 $\mu g/m^3$ the limit is 1%. Below the gray area: 10% is the tolerable error probability.

1.2.7 Optimize the Design for Obtaining Data

Review the Data Quality Objective Outputs and Existing Environmental Data - The TAG will review the data quality objectives (DQOs) and Fumigant Sampling and Analysis Plan, in addition to the DQO outputs. Monitoring data from Phase One showed a maximum 12-hr concentration of 1 $\mu g/m^3$ of MITC. The maximum 24-hr concentration was 0.75 $\mu g/m^3$. (No other fumigants were monitored during Phase One.) The estimated population 99.98th percentile in Phase One was 4.2 $\mu g/m^3$. The overall CV was 200%. Other monitoring data indicate air concentrations vary with numerous factors such as distance from the application, time after application, application rate, acreage, method of application, and meteorological conditions.

Develop General Data Collection Design Alternatives -
<u>Simple Random Sampling -</u>
For the present study, Simple Random Sampling would involve choosing the sample locations by selecting points randomly in three spatial dimensions (i.e. latitude, longitude, and height), and choosing the sample starting times randomly within the study period.
<u>Systematic Sampling -</u>
Systematic Sampling would involve choosing the sampling locations at evenly spaced distances in the three spatial dimensions, and choosing the sample times at evenly spaced

intervals.

Stratified Random Sampling –

Stratified Random Sampling would divide the study area into distinct subareas with different, known probabilities of having the highest 24-hr concentration. Similarly, the study period would be divided into subperiods with different, known probabilities of having the highest 24-hr concentration. A predetermined proportion of the total samples would be randomly selected from seach subarea/subperiod combination, with the proportion depending on the probability of highest concentrations in that combination.

Formulate the Mathematical Expressions Needed to Solve the Design Problem for Each Data Collection Design Alternative –

Because of the practical constraints on the location and scheduling of sampling events, none of the three design alternatives outlined can be implemented. Because it is desirable to maximize the probability of capturing peak concentrations, and because peaks are expected to be associated both spatially and temporally with fumigant applications, neither Simple Random Sampling nor Systematic Sampling would be very efficient. Stratified Random Sampling would be preferred, if the data existed to define the strata. Since they do not, the sampling strategy that will be used is a qualitative approximation to Stratified Random Sampling. Existing monitoring data are not adequate to characterize statistically the spatial and temporal distribution of peak concentrations. Instead, the monitoring sites and times chosen are those expected to have the highest concentrations based on past fumigant application patterns and meteorological data.

Select the Optimal Sample Size that Satisfies the DQOs for Each Data Collection Design Alternative –

The study design is not statistically based, and therefore, no statistical methods for estimating precision or power are exactly applicable. Statistical methods for Simple Random Sampling have been used to evaluate the planned study design, but the use of these methods must be considered as approximate and providing guidelines only.

The planned study design calls for a total of 75 24-hr samples for MITC (5 sites times 5 applications times 3 days per application).

Previous ambient monitoring has not been coordinated with applications of fumigants, so the data do not contain information about the magnitude of variability between applications. It is therefore not possible to determine a statistically optimal number of applications to monitor. Given the limited number of applications expected to occur in the study area, the study plan to monitor 5 applications per fumigant is likely to capture all applications.

Because of the absence of data on inter-application variability, it is not possible to determine an optimal number of samples per application. Instead, the sample size calculations are based on the total number of days monitored per site. That is, 5 applications times 3 days per application is treated as identical with 3 applications times 5 days per application.

For acute effects, the null hypothesis is that the maximum 24-hr concentration is greater than or equal to the acute screening level of 66 $\mu g/m^3$ (for MITC). The statistical test will be to reject H_0 if the maximum value is less than some critical value. Computer simulation was used to construct the null distribution of the estimator. Because ambient air concentrations typically have a lognormal distribution, and because the true maximum value in a lognormal distribution is undefined (being infinite), the null and alternate distributions were defined in terms of the population 99.98th percentile. Assuming that 24-hr average concentrations from the pooled sites have a lognormal distribution whose true 99.98th percentile equals 66 and whose CV is 200% (the overall CV in the 1998 monitoring data), the parameters $\mu = -0.236$ and $\sigma = 1.268$ were found by solving the equations for the CV and 99.98th percentile of a lognormal distribution.

$$CV = 2.0 = \sqrt{\exp\{\sigma^2\} - 1} \quad , \text{ and } \quad 99.98th\ percentile = 66 = \exp\{\mu + 3.49\sigma\}.$$

Ten thousand sets of 75 samples from the parent population were simulated and the maximum value found in each set. The null distribution is the distribution of the 10,000 values of the maximum. The 5th percentile of the null distribution is the critical value for the test of the null hypothesis at the α=0.05 level. This value was determined to be 7.4

μg/m^3.

The power of the test against alternate hypotheses was calculated by simulating 10,000 sets of 75 values from lognormal distributions with a CV of 200% and 99.98th percentiles equal to 6.6, 10, 20, 30, 40, 50, 60 or 100 μg/m^3. In each of the 10,000 sets, the null hypothesis that the maximum is greater than or equal to the screening level was tested by comparing the observed maximum to the critical value. The power of the test is the proportion of times that the null hypothesis was rejected.

Power of the alpha-level 0.05 test of
H_0: Maximum 24-hr concentration $\geq$ 66 μg/m^3
against alternative hypotheses (n=75).

True value of 99.98th %ile (μg/m^3)	Power
66	0.05
60	0.08
50	0.17
40	0.32
30	0.53
20	0.77
10	0.96
6.6	0.99

The power calculations indicate that if the samples were randomly selected, and they came from the hypothetical lognormal population, 75 would be an adequate number of samples. Because the random sampling requirement cannot be met, however, these calculations can only be considered roughly approximate. In light of that, DPR proposes to use the slightly more health-protective value of 1/10 the screening level as the critical value for the hypothesis test, and in addition is suggesting the three-level decision rule: if the observed maximum concentration falls below the screening level but above one order of magnitude below the screening level, a more refined analysis will be undertaken to determine whether air levels are safe (Table 1).

Select the Most Resource-Effective Data Collection Design that Satisfies All of the DQOs – Because the study design is dictated by practical constraints and data limitations, there is no choice to be made here.

Document the Operational Details and Theoretical Assumptions of the Selected Design in the Sampling and Analysis Plan – The chosen design is expected to give the highest probability of detecting the maximum fumigant concentration with the available resources. Three sampling sites will be established on the west side of Lompoc, closest to the agricultural area and where the highest concentrations are expected. One site will be located in the northwest corner of Lompoc, one on the center-west side, and one in the southwest corner (Fig. 3). An additional site will be located near the central part of Lompoc, as recommended by the Air Resources Board and the U.S. Environmental Protection Agency staff involved with this study. In addition, the location of a sampling site on the eastern edge of town was raised before the TAG. There are some fumigants applied to fields in this region, although fewer than the applications that occur on the west side of the city. However, in an effort to capture potential influx of fumigants from eastern applications, a fifth site is located in the north-east region of Lompoc.

Monitoring locations were selected to represent the portion of the city that would likely have the highest fumigant concentrations, given the location of applications and general wind patterns in the valley. Modeling potential fumigant concentrations in the city to help locate air-sampling locations was not conducted. The possibility of conducting this type of modeling was discussed with technical staff from the Air Resources Board, U.S. EPA, and the California Department of Pesticide Regulation at a meeting held on Oct. 5, 1999 in Sacramento. It was decided by meeting participants not to model potential air concentrations in Lompoc due to: 1. the uncertainty and variability in model-input data, 2. the amount of time required to make multiple model runs of even a small fraction of the potential application and wind pattern combinations, and 3. the inability for modeled outputs to pinpoint the one site expected to have the peak concentration.

Monitoring will occur during a high use period as indicated by pesticide use reports. The number of applications that will occur during this period is unknown; some fumigants may not be applied at all. Up to 13 applications will be monitored.

2. SITE DESCRIPTION

2.1 Topography

The City of Lompoc is a small city located in a coastal valley of Santa Barbara County, California (Figure 1). The population has been estimated at 37,649 in a U.S. Census conducted in 1990. The city is located approximately seven to eight miles east of the coastline. The valley is oriented roughly northwest to southeast and the surrounding hills form a V shape fanning out towards the ocean. Hills to the east of Lompoc tend to stall air movement as it passes the city, while the air is funneled eastward through the Santa Ynez River basin. Vandenberg Air Force Base (a rocket launch facility) and agricultural fields dominate the area between Lompoc and the coast. Five major crops or crop groups are grown in this area: cole crops (broccoli, cabbage, and cauliflower), lettuce, dried beans, celery, and flowers.

2.2 Climate

The region is dominated in summer months by a Pacific high-pressure area. This high-pressure area tends to produce northwesterly winds in the Lompoc area. Aiding this tendency, the Central Valley of California heats up during the summer and creates a large pressure and temperature differential between inland and ocean surfaces. The air aloft from the Pacific high is generally warming and descending as it approaches the coastline near Vandenberg Air Force Base. Consequently, the cool moist marine area below tends to form a subsidence inversion accompanied by frequent fog or low cloudiness. The northwesterly winds exert pressure on the ocean surface that causes up-welling of cool water. This cools the air near the surface and contributes to fog formation. During winter, the Pacific high weakens, the jet stream shifts southward, and heating of the Central Valley is weaker or absent. Winds tend to be more westerly and frontal systems move through the area, changing the wind direction more frequently than in summer months. This summary and a complete description of weather patterns for Lompoc are given in Johnson, 1998.

2.3 Pesticide Use

The information given in this section was extracted from DPRs pesticide use report database. Data for 1996 and 1997 are complete and validated. As of July 1999, data for 1998 are complete, but not yet validated. A complete description of the pesticide use report database is given in DPR, 1995.

Between 1996 and 1998, approximately 120 pesticides have been used for agricultural production in the Lompoc area, with approximately 120,000 pounds used per year. Consistent with the crops and climate, insecticides and fungicides are the most heavily used pesticides in the Lompoc area. The pesticides used in the greatest amounts for agricultural production are shown in Table 1.

Fumigants are a unique class of pesticides. They are highly volatile, applied infrequently, but at higher rates than other pesticides (50 to 400 pounds per acre), and used to control a wide variety of pests and diseases. Between 1996 and 1998, there were 81 applications of the fumigant metam-sodium, six of methyl bromide/chloropicrin, and one of 1,3-dichloropropene, compared to approximately 2000 for the insecticide chlorpyrifos (Table 2, DPR 1996, 1997a, and 1998). However, the 88 fumigant applications accounted for almost 92,000 pounds of the 360,000 total pounds of pesticides. Fumigants are applied prior to planting. Therefore, many applications occur during the fall and winter (Table 3). In the Lompoc area, most fumigants are injected underground by tractors, and occasionally through drip irrigation systems. Because of their high volatility and high application rates, fumigants are the focus of the monitoring described here.

3. PREVIOUS INVESTIGATIONS

3.1 Study of Hospital Discharges

The hospital discharge data from 1991-1994 suggest that certain respiratory illnesses occur in Lompoc at higher rates than in other comparison areas. The State's Office of Environmental Health Hazard Assessment evaluated this data (Wisniewski et al., 1998; Ames and Wisniewski, 1999). The evaluation indicated that the proportion of hospitalizations due to respiratory illnesses, in particular bronchitis and asthma, were elevated in Lompoc relative to the proportion of hospitalizations in the comparison areas, with some differences by age. The incidence of lung and bronchus cancers also was increased above the expected numbers based on regional rates. The purpose of the report was not to speculate on the cause of the illnesses; rather, it was to evaluate the incidence of specific illnesses.

3.2 Phase One of Pesticide Air Monitoring

The Phase One study was intended to test pesticide sampling and analysis methods and to determine if a subset of the total pesticides in use in the area could be measured in air. With some exceptions, these goals were achieved. The study was most successful in developing and demonstrating the multiple-pesticide sampling and analysis method. Due to the limited nature of the Phase One sampling, these results are not appropriate for risk assessment.

Over 50 pesticides were used in or near Lompoc during the August-September 1998 monitoring period. Air monitoring was conducted for twelve pesticides with recorded use in those months in prior years. Of the 12, five were not applied during the 1998 monitoring period, and were not detected in air samples. The remaining seven were detected in air samples. Many of these detected concentrations were between the sample detection limit and quantitation limit meaning that the existence of the pesticide in a sample, while likely, was too low to be assigned a numerical value. For example, chlorpyrifos, the most frequently detected pesticide, was detected in 55 of 119 samples above the quantitation limit of 4 ng/m^3, and in an additional 60 of 119 samples between the quantitation limit and the detection limit of 1 ng/m^3.

The results for MITC (the biologically-active breakdown product of metam-sodium) are estimates due to poor quality assurance/quality control of the samples. Qualitatively, the results probably represent an underestimate of the MITC actually present in the samples. The highest concentrations of MITC were the result of one application of 720 pounds of metam-sodium on 7.5 acres approximately one mile west of Lompoc.

Cycloate was not one of the 12 pesticides on the monitoring list, but was detected during laboratory screening. Concentrations of cycloate are considered to be estimates because of limited laboratory quality assurance.

The metal analyses were originally intended as surrogates for pesticides containing metals (aluminum in fosetyl-Al, and manganese in maneb and mancozeb). In retrospect, these analyses are not capable of discriminating between pesticide applied sources and natural background sources, e.g. soils. Results should not be interpreted as indicative of the presence or absence of these metal-containing pesticides in air.

Silicon was tested for and found in Lompoc air during the monitoring period. Levels were found as high as 17,000 ng/m^3, the highest level measured in any California urban area in 1994.

3.3 Air Concentrations of Fumigants Measured in California

1,3-dichloropropene was measured in Merced County in April 1990 using coconut based charcoal sorbent and analyzed by gas chromatography and an electron capture detector

(Baker et al., 1996). Four sites were measured over the course of eight days and all concentrations were above the minimum quantitation level of 0.10 ug/m^3. The maximum concentration was 160 ug/m^3, the average was 24 ug/m^3, and the mean urban background concentration was 0.90 ug/m^3.

Chloropicrin was measured in Monterey County in September 1986 using XAD-4 resin and analyzed by gas chromatography and an electrolytic conductivity detector (Baker et al., 1996). Three sites were measured over the course of 16 days with 28% of the samples above the minimum quantitation level of 0.085 ug/m^3. The maximum concentration was 4.6 ug/m^3, the average was 0.64 ug/m^3, and the mean urban background concentration was <0.085 ug/m^3.

MITC was measured in Kern County in July 1993 using coconut based charcoal sorbent and analyzed by gas chromatography and a nitrogen-phosphorous detector (Baker et al., 1996). Four sites were measured over the course of eight days with 83% of the samples above the minimum quantitation level of 0.01 ug/m^3. The maximum concentration was 18 ug/m^3, the average was 5.8 ug/m^3, and the mean urban background concentration was 2.1 ug/m^3.

Methyl bromide was measured in Monterey County in September 1986 using petroleum based sorbent and analyzed by gas chromatography and an electron capture detector (Baker et al., 1996). Three sites were measured over the course of 16 days with 1% of the samples above the minimum quantitation level of 4.2 ug/m^3. The maximum concentration was 4.4 ug/m^3, the average was 4.1 ug/m^3, and the mean urban background concentration was <4.2 ug/m^3.

4. SAMPLE COLLECTION DESIGN

The design for sample collection is a product of the DQO process as well as a result of community and technical input from the TAG and LIWG. This section describes the types of samples to be collected, sample measurement details, numbers of sampling sites and their general location, and other information pertinent to field collection and shipment of samples.

4.1 Safety

Sampling of air in the city of Lompoc does not pose an occupational hazard for the sampling crew. However, there is a concern for sampling crew safety. Air samplers are located on rooftops for sample security purposes and access to the roofs is by ladder. Due to the lack of safety guardrails on the rooftops, air sample changes will be restricted to daylight hours. Sunrise on the shortest day of the year in December is approximately 7:05 A.M. and sunset is approximately 4:55 P.M. In addition, it takes approximately two hours to change the tubes at five sites. For that reason, air sample changes during this study will be conducted at a mean time of 8:00 A.M. and 4:00 P.M. Therefore, field staff will commence daylight sampling at the first site at 7:00 A.M. and finish roughly at 9:00 A.M. and commence nighttime sampling at 3:00 P.M. and finish roughly at 5:00 P.M.

An additional safety consideration is sampling during rainfall events. Due to slick surface conditions on rooftops and the lack of guardrails, sampling will not be conducted when it rains. In the event of a light rain or drizzle, field-sampling staff will proceed with sampling if they are confident it is safe to do so.

4.1 Sampling Theory

In Phase One sampling, five sites were used to monitor air concentrations in Lompoc (Fig. 1). In discussion with the TAG on October 26, 1999, a sampling plan was formulated based on study objectives and monetary constraints. The TAG decided to monitor the original five sites. The sites of primary concern were those along the western edge of the city due to proximity to the majority of the agriculture in the valley and the predominance of wind directions from the west and northwest. During the months of November through January, the winds are from the west and northwest just over 50% of the time (Figure 2). The group decided to coordinate sampling with specific applications that occur in the valley, meaning when an application occurs, monitoring will begin. Based on historical information from flux of each of the fumigants, the highest concentrations measured around treated fields tend to occur within three days of application (ARB 1987; Ross et al. 1996; Beard 1994; Fitzell 1993). Therefore, three days of sampling was recommended for monitoring in an attempt to capture peak air concentrations which residents in Lompoc might be exposed. Due to historical problems with breakthrough of some of the fumigants at long sampling intervals (greater than 12 hours), two samples will be collected during a single 24-hour period to estimate a 24-hour acute exposure. Therefore, for any given fumigation event, a minimum of 30 samples will be collected. Add to this 3 duplicates, two trip spike, two trip blanks, and two field spikes, yields 39 samples per fumigation event for the primary laboratory. This does not include any continuing quality control samples run in the laboratory. The TAG agreed that as many fumigation events as possible should be sampled.

At its March 19, 1999 meeting, the TAG and LIWG agreed to the following budget for fumigant monitoring:

Primary laboratory analysis	$60,000
Quality Control	6,000
Second laboratory	6,000
Field sampling	10,000
Mini-Sodar met station	16,000
Miscellaneous costs	2,000

At its October 26, 1999 conference call, the TAG agreed to the following revised budget:

Primary laboratory analysis	$80,000
Quality Control	included in cost of primary lab
Second laboratory	provided at no charge by DPR and EPA
Field sampling	20,000
Mini-Sodar met station	redirected to sampling and analysis
Miscellaneous costs	0

The field and laboratory contracts charge personnel and operating expenses against this budget, as opposed to per sample charges. Method development and validation by the primary laboratory cost approximately $40,000. Each application monitored costs between $1500 - $2000 for field sampling and $3000 - $4000 for laboratory analysis. Between 10 and 13 fumigant applications can be monitored with the available funds.

The distribution of the number of fumigations to be monitored for each fumigant was based on the historical number of applications made for each fumigant (Tables 3 and 4). Therefore, the numbers of fumigations to be monitored: one to two for 1,3-dichloropropene, one to two for chloropicrin/methyl bromide, and five to eight for metam sodium. (Note, chloropicrin and methyl bromide are combined in the formulated fumigant products used in Lompoc, but have to be analyzed separately due to differences in sampling and analytical measurement requirements.) If eight metam-sodium applications are monitored before any 1,3-dichloropropene or chloropicrin/methyl bromide applications are monitored, the TAG will meet to determine which future applications should be monitored.

Statistical power calculations (see Section 1.2.7) indicated that if the samples were randomly selected from a lognormal population, 45 24-hr samples per fumigant would be an adequate number for testing the null hypothesis. They further indicated that little power is gained by increasing the number of samples. Because the random sampling requirement cannot be met, however, these calculations can only be considered approximate.

4.2 Sampling Method

This section will describe two field-sampling methods that will be used to measure air concentrations of the four fumigants. The first method uses sorbent tubes to trap the fumigants and sampling and chemical analytical methods have been established for all four fumigants. The second sampling method uses canisters to trap air followed by chemical analysis of the gas inside the canister. Currently, methods for two of the four fumigants are available using canisters.

4.2.1 Sorbent Tubes

The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith 1988). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel 1995; Keith 1988; Baker, et al. 1996).

4.2.2 Canisters

Canisters have been used as an alternative to solid sorbents for air sampling (Keith 1988). In addition, a study by Biermann and Barry (1999) indicated that methyl bromide recovery from canisters was significantly higher than recovery from charcoal sorbent tubes. For this reason, U.S. EPA staff recommended use of canisters for <u>all</u> fumigants to be monitored in this study. However, at this time, chemical analytical methods are only available for two of the four fumigants (1,3-dichloropropene and methyl bromide) using canisters as the air sampling method. A third method for MITC is under development at the primary laboratory and might be completed by the end of November 1999. A method for chloropicrin is not available at this time.

4.3 Sample Type

Air samples will be run for consecutive 8- and 16-hour intervals during the course of a 24-hour day. For safety reasons, the change of air sampling tubes and canisters will occur in daylight hours. The 8-hour daytime sample will commence at 7:00 A.M. at the first site. The 16-hour nighttime sample will commence at 3:00 P.M. at the first site. This sequence of air sampling tube changes will continue until three days have been completed (72 hours of sampling).

4.4 Media

In addition to air, meteorological measurements of wind speed, wind direction, temperature, and relative humidity will be made. See section 4.13 for meteorological sampling details.

4.5 Collection Schedule

Certain pesticides are designated restricted materials. One of the requirements for use of restricted materials is that the county department of agriculture be informed by the applicator prior to application. All of the fumigants that will be monitored are restricted materials. The Santa Barbara County Department of Agriculture will inform sampling personnel when a fumigant application is scheduled for the Lompoc area, as defined by the agricultural region outlined in Figure 3. For each fumigation event, sampling will commence within 24 hours of notification by the Agricultural Commissioner's Office that an application will occur. For example, if field-sampling staff receive notice on Tuesday that an application will occur on Wednesday during the daytime, field sampling will begin at 7:00 A.M. on Wednesday. If field-sampling staff receive notice on Saturday that an application will occur Sunday night, monitoring will commence Sunday at 3:00 P.M. In summary, monitoring will commence with the daytime or nighttime period during which the application is scheduled to occur.

A maximum of 13 fumigant applications will be monitored: two 1,3-dichloropropene, two chloropicrin/methyl bromide, and five metam-sodium applications are the minimum agreed to by TAG members in March 1999. As fumigations proceed, members of the TAG will be consulted concerning which fumigant applications to focus. These 13 fumigant applications will be monitored from November 1999 through January 2000. The possibility of extending monitoring into April is being explored with TAG members, and laboratory and field contractors. For each fumigant application monitored, six sequential samples will be collected at each site, as described in 4.3 above. A schedule for sample collection is in Appendix F.

4.5.1 Schedule for Quality Control Field Sampling

In addition to field samples collected during a fumigation event, three duplicate (co-located) samples, two fortified spikes, four trip spikes, two trip blanks, and three confirmation samples will be collected. The three duplicate samples will be analyzed by the primary laboratory, as will the two fortified spikes. Two of the four trip spikes and both trip blanks will also be analyzed by the primary laboratory. The remaining samples, two trip spikes and three confirmation samples, will be analyzed by the confirmation laboratory. The location of duplicate samples, fortified samples, and confirmation samples was randomly assigned using a random numbers table and a unique number assigned to each sampling interval at each site (Appendix F). A fortified spike (also called a sample spike) is a laboratory spike prepared as soon as the primary laboratory is notified of a fumigation. This spike is then sent to the field, placed on an air sampler with air flowing through the sorbent tube. It is treated just like a field sample. A trip spike is a laboratory spike that is prepared when the primary laboratory is notified of a fumigation. The trip spike accompanies field samples while in temporary storage and during shipment to the laboratory.

The need for trip spikes and blanks for canisters will be decided upon in consultation with the primary and secondary laboratories.

4.6 Sampling Site Locations

Monitoring will occur at four sites within the city of Lompoc, one each in the northwest, central-west, southwest, and near the center of Lompoc (Figure 3). These sites were also used for Phase One. All locations meet the U.S. EPA siting criteria for ambient air monitoring sites (Appendix D). Samplers at all locations are on rooftops to ensure the security of the samples. As an extra measure of security, members of the TAG requested that the exact street address of these sites not be included in sampling-plan documents.

4.7 Preparation for Sampling

Sample labels with the study number and sample identification number will be attached to all sampling tubes and canisters before delivery to field sampling staff. Chain of custody forms, sample analysis request forms and a data log book will be supplied to field sampling staff. Samplers will be pre-calibrated in the laboratory for the flow rates required for air sampling. Permission for access to sampling sites has been confirmed at four of the five locations. A storage unit will be rented to house equipment and samples temporarily stored on dry ice. All equipment necessary for monitoring will be delivered to Lompoc and set-up prior to fumigation monitoring. Fumigation monitoring will not begin until formal approval for such activity is received from US EPA.

A MetOne meteorological station will be placed approximately one mile west of Lompoc (Figure 1). The station will be operational prior to the start of monitoring. Meteorological data will be collected during the course of the entire monitoring period (November through January, and longer if sampling continues beyond January).

4.8 Equipment

Equipment to be delivered to field sampling staff

Record book
Data Log Book
SKC INC. personal samplers
AC adapters
Sampler support system
Rotameters
Flow Calibrators
Sample tubes; XAD-4 tubes, petroleum charcoal tubes, coconut charcoal tubes
Chain of custody forms
Request for analysis forms
Caps for tubes
Security Seals
Connectors for tubes
Tube breakers
MetOneb meteorological station
Campbell Scientific micrologger and storage modules
Compass
Allen wrenches
Spanner wrench
Anemometer
Sling psychrometer
Hand-held Thermometer
HobobTemp Temperature Data loggers
Ice chests or freeze-safes

Duct tape
Dry ice (to be purchased as needed)

Additional AC adapters are on order but all other equipment is available and operational.

4.9 Field Tests

Prior to field sampling, a fortified sample will be run. The primary laboratory will generate a minimum of four spikes and mail, overnight mail, to DPR staff. A minimum of two samples will be run on air samplers for 16 hours. The samples will be shipped within 12 hours of sample collection, overnight mail, back to the primary laboratory. This trial run is being preformed to test shipping procedures, fortified spike procedures, accuracy of paperwork completion, and trapping efficiency of sorbent tubes.

In addition to the above trial run, a field test run is recommended to identify any potential problems in the sampling procedure. The field technician will run through the entire procedure involved with one sampling interval, from sample placement through sample removal, temporary storage, and shipping to the appropriate laboratories. If approved by US EPA, samples collected during this trial run will also be analyzed as background samples. The schedule for background sampling is included in Appendix F. The analyte for background sampling will be MITC.

The MetOne meteorological station will be checked once a month against hand-held sensors. Storage modules will be exchanged and downloaded approximately once a month.

Air sampling pumps will be calibrated in the laboratory prior to monitoring. In addition, flow rates will be checked in the field before and after each sampling interval with a rotameter. Rotameters are checked against a flow calibrator in the laboratory.

4.10 Field Testing Procedure References

The use, operation, calibration and maintenance of air sampling pumps are described in DPR’s SOP EQAI001.00 (Appendix G). Preparation of sorbent tubes for use with air sampling pumps is described in DPR's SOP FSAI001.00 (Appendix G). Preparation and usage of temperature data loggers that are placed in ice chests to record temporary storage and transport temperatures are described in DPR's SOP EQOT001.01 (Appendix G). The meteorological station will be set up according the DPR SOP EQWE001.00 (Appendix G).

4.11 Sample Collection References

Sorbent tube samples will be collected according to procedures listed in DPR SOP EQAI001.00 (Appendix G). Canister air samples will be collected according to US EPA Method TO-15 (US EPA, 1997). Instructions for field sampling personnel are detailed in DPR's abbreviated protocol for air monitoring in Lompoc (Appendix F). Chain of custody forms, log book sample form, laboratory analysis request form, canister sampling data sheet and canister check-in sheet are appendices in DPR's air monitoring protocol (Appendix F). Canister cleaning methods (US EPA region 9 SOP #312) is also in Appendix G.

4.12 Shipment of Samples

Samples will be shipped via UPS Overnight. The samples will be packaged and shipped according to procedures in DPR's SOP QAQC004.1 (Appendix G). Each shipment of samples will be accompanied by a temperature data-logger to record sample temperatures from collection to delivery to the lab. Shipment of samples will be scheduled as soon as possible after final sample collection for fumigation event. Sample shipment should be timed such that samples will not arrive in the laboratory on a weekend or holiday.

4.13 Meteorological Sampling

A MetOne meteorological station will be set up at a site near the agricultural areas on the west side of the city of Lompoc. The station will be set up according the DPR SOP EQWE001.00 (Appendix G). The MetOneb meteorological sensors will be placed on a trailer mast at a height of 10 meters. The sensors will record wind direction, horizontal wind speed, temperature, and relative humidity. The MetOneb sensors were calibrated by the manufacturer on October 5, 1999 to fit within the specifications of the manufacturer. The meteorological data will be recorded on a Campbell Scientific CR 21X Datalogger every 15 minutes as per USEPA Guidelines on air quality models (revised), (see Appendix W of 40 CFR part 51 EPA-450/2-78-027R).

4.14 Pesticide Use Data

Pesticide use data will be collected from pesticide use reports submitted by growers to the County Agriculture Commissioner's office. Universal use reporting required by the state of California, directs all growers to submit details of pesticide usage on a monthly basis. This is the only state in the United States which requires such records.

As part of general enforcement procedures, staff from the Agriculture Commissioner's Office are required by law to perform inspections of 5% of all sites identified in permits or notices of intent to apply a pesticide for an agricultural purpose (3 CCR 6436). These inspections are performed on a non-appointment basis and cover various aspects of pesticide use such as compliance with permit and label requirements, application equipment inspections, mix/load inspections, and field-worker safety inspections. Department of Pesticide Regulation manual (DPR 1997b) details procedures enforcement staff use to assure grower compliance with pesticide labels and state and federal laws regarding pesticide use.

Additional procedures for this study will include verification of the date, time, and location (Township-Range-section) of fumigant application by the Agriculture Commissioner's staff. Verification will be performed either by phone or site visit. Staff at DPR will be notified of the date, time, and location of fumigation as soon as possible.

5. SAMPLE ANALYSIS DESIGN

5.1 Constituents of Interest

The constituents of interest are the fumigants 1,3-dichloropropene, chloropicrin, and methyl bromide. In addition, the biologically active breakdown product of metam sodium, MITC will be measured due to the short half-life of metam sodium and its low volatility (Table 7). MITC is the biologically active product for soil fumigations. Field research has demonstrated that 87 to 95% of the applied metam sodium degrades to MITC in various soils tested (Smelt et al., 1989; Burnett and Tambling, 1986; Gerstl et al., 1977; Leistra et al., 1974; Leistra, 1974; Smelt and Leistra, 1974; Turner and Corden, 1963). The conversion exhibited a half-life of less than 30 minutes to seven hours, and varied with soil conditions. Certain degradation products have been theorized or actually measured in air (Wales, 1999; Moilanen et al., 1978; Woodrow et al., 1983; Carter et al., 1997, Table 7). However, due to budgetary constraints, air measurement of additional atmospheric constituents cannot be addressed in this study.

5.2 Sample Preparation References

Chemical extraction methods for 1,3-dichloropropence and methyl bromide from sorbent tubes and removal from canisters are referenced below for the primary and confirmation laboratories. Chemical extraction methods for chloropicrin and MITC from sorbent tubes are referenced below for the primary and confirmation laboratories. (Note: At the time of this writing there were no analytical methods for chloropicrin and MITC sampled using canisters.)

5.2.1 Chemical extraction methods for 1,3-dichloropropene from sorbent tubes

The primary laboratory- Extraction for 1,3-dichloropropene from sorbent tubes will be performed in accordance with the SOP in Appendix H.
The confirmation laboratory- Extraction for 1,3-dichloropropene from sorbent tubes will be performed in accordance with the SOP in Appendix I.

5.2.2 Removal of 1,3-dichloropropene from canisters

The primary laboratory- An aliquot of air is removed from the canisters as described in

the SOP in Appendix J.
The confirmation laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.

5.2.3 Chemical extraction methods for chloropicrin from sorbent tubes

The primary laboratory- Extraction for chloropicrin from sorbent tubes will be performed in accordance with the SOP in Appendix L.
The confirmation laboratory- Extraction for chloropicrin from sorbent tubes will be performed in accordance with the SOP in Appendix M.

5.2.4 Chemical extraction methods for MITC from sorbent tubes

The primary laboratory- Extraction for MITC from sorbent tubes will be performed in accordance with the SOP in Appendix N.
The confirmation laboratory- Extraction for MITC from sorbent tubes will be performed in accordance with the SOP in Appendix O.

5.2.5 Chemical extraction methods for methyl bromide from sorbent tubes

The primary laboratory- Extraction for methyl bromide from sorbent tubes will be performed in accordance with the SOP in Appendix P.
The confirmation laboratory- Extraction for methyl bromide from sorbent tubes will be performed in accordance with the SOP in Appendix Q.

5.2.6 Removal of methyl bromide from canisters

The primary laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix R.
The confirmation laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.

5.3 Analysis Procedure References

Chemical analytical methods for 1,3-dichloropropence and methyl bromide from sorbent tubes and canisters are referenced below for the primary and confirmation laboratories. Chemical analytical methods for chloropicrin and MITC from sorbent tubes are referenced below for the primary and confirmation laboratories. (Note: At the time of this writing there were no analytical methods for chloropicrin or MITC trapped in canisters.)

5.3.1 Chemical analytical methods for 1,3-dichloropropene extracted from sorbent tubes

The primary laboratory- Analytical methods for 1,3-dichloropropene extracted from sorbent tubes will be performed in accordance with the SOP in Appendix H.
The confirmation laboratory- Analytical methods for 1,3-dichloropropene extracted from sorbent tubes will be performed in accordance with the SOP in Appendix I.

5.3.2 Chemical analytical methods for 1,3-dichloropropene removed from canisters

The primary laboratory- Analytical methods for 1,3-dichloropropene removed from canisters will be performed in accordance with the SOP in Appendix J.
The confirmation laboratory- Analytical methods for 1,3-dichloropropene removed from canisters will be performed in accordance with the SOP in Appendix K.

5.3.3 Chemical analytical methods for chloropicrin extracted from sorbent tubes

The primary laboratory- Analytical methods for chloropicrin extracted from sorbent tubes will be performed in accordance with the SOP in Appendix L.
The confirmation laboratory- Analytical methods for chloropicrin extracted from sorbent tubes will be performed in accordance with the SOP in Appendix M.

5.3.4 Chemical analytical methods for MITC from sorbent tubes

The primary laboratory- Analytical methods for MITC extracted from sorbent tubes will be performed in accordance with the SOP in Appendix N.
The confirmation laboratory- Analytical methods for MITC extracted from sorbent tubes will be performed in accordance with the SOP in Appendix O.

5.3.5 Chemical analytical methods for methyl bromide extracted from sorbent tubes

The primary laboratory- Analytical methods for methyl bromide extracted from sorbent tubes will be performed in accordance with the SOP in Appendix P.
The confirmation laboratory- Analytical methods for methyl bromide extracted from sorbent tubes will be performed in accordance with the SOP in Appendix Q.

5.3.6 Chemical analtyical methods for methyl bromide removed from canisters

The primary laboratory- Analytical methods for methyl bromide removed from canisters will be performed in accordance with the SOP in Appendix R.
The confirmation laboratory- Analytical methods for methyl bromide removed from canisters will be performed in accordance with the SOP in Appendix K.

5.4 Initial Quality Control Requirements

Initial quality control consists of a standards check, verification of calibration, the method detection limit determination, and analysis of matrix spikes.

5.4.1 Standards Check

Each laboratory uses certified standards. The primary and quality control laboratories will exchange standards for each analyte for verification. The primary and quality control laboratories will also exchange standards at the end of the study. New standards are prepared at least every six months. New standards are compared with old standards for verification. Standards for fumigants have shown no degradation over a six-month period in prior studies.

5.4.2 Verification of Calibration

Both the primary and quality control laboratories verify calibration by analyzing a series of standards (samples containing known amounts of analyte dissolved in a solvent for the sorbent samples or air for the canister samples). The linear range of calibration is determined by analyzing standards of increasing concentration. Within the linear range, the calibration is determined by regressing the standard concentration on the response of the instrument (peak height or peak area of the chromatogram) using at least five concentrations. The minimum acceptable correlation coefficient of the calibration is given in the SOP for each method, but in general is at least 0.95. The calibration is verified with each set of samples analyzed as described in section 6.4 for continuing quality control.

5.4.3 Method Detection Limit

Each laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. This standard is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA 1990. The method detection for each analyte and method is given in the SOP.

5.4.4 Analysis of Matrix Spikes

A series of matrix spikes (sorbent tube samples containing known amounts of analyte) were analyzed to determine the precision and accuracy of the methods. Each laboratory analyzed at least ten matrix spikes at various concentrations. The mean recovery and standard deviation were calculated for each method. Data for the matrix spikes are given in the SOP for each method. The precision and accuracy are verified with each set of samples analyzed as described in section 6.4 for continuing quality control.

5.5 Laboratories

The primary laboratory for all four analytes, for all methods of sample collection, is the California Department of Health Services, Environmental Health Laboratory located at 2151 Berkeley Way, Berkeley, California 94704. The confirmation laboratory for all four analytes trapped with sorbent tubes is the California Department of Food and Agriculture, Center for Analytical Chemistry located at 3292 Meadowview Road, Sacramento, California 95832. The confirmation laboratory for all analytes trapped using canisters (i.e. 1,3-dichloropropene and methyl bromide, only) is the U.S. Environmental Protection Agency, Region 9 Laboratory located at 1337 S. 46th Street, Building 201, Richmond, California 94804.

5.6 Sample Transit Conditions

Immediately following sample collection, all air samples collected using sorbent tubes will be placed in a cooler or freeze safe containing ample quantities of dry ice (see section 4.12 for details of sample shipment conditions). Upon arrival in the analytical laboratories and after sample check-in procedures, samples will be placed in secure freezers kept at -4C or below. Canisters do not require special temperature conditions during sample handling or shipment.

5.7 Holding Times

Sample holding times are specified for each analyte - sample collection combination using storage stability measurements and expected number of days that will pass between sample collection and sample arrival in the laboratory. Sample holding times for all fumigants trapped with sorbent tubes or canisters is 14 days.

5.8 Trapping Efficiency

The trapping efficiency for each fumigant trapped on sorbent tubes is listed in Table 5.

5.9 Limit of Quantitation

The limits of quantitation for each fumigant from sorbent tubes and canisters are listed in Table 5.

6. DATA VALIDATION/QUALITY ASSURANCE

6.1 Sample Receipt Verification

Sample receipt, log-in, and verification procedures for each laboratory are in Appendix S.

6.2 Holding Time Verification

Holding times will be verified by date of sample collection and date of extraction listed on the chain of custody records and laboratory reports. Verification will be ensured in the laboratory by the lead chemist assigned to the project and also checked by the study director at DPR.

6.3 Audit Results

The quality assurance (QA) team for this project, led by staff from the California Air Resources Board submitted a questionnaire to all three laboratories participating in this study. Subsequent to mailing this questionnaire, the QA team visited each laboratory for an audit prior to study commencement. The audit resulted in a list of items that will assist the laboratories in their efforts to have quality data. The list of items submitted is in Appendix T and have been addressed in this sampling plan.

In addition, the QA team will schedule another audit during sample analysis in each of the laboratories.

In addition, members of the TAG requested a field flow audit. The ARB team leader will not be available for such an audit, but US EPA staff might be able to provide this service.

6.4 Quality Control Results

A five-point calibration curve, minimum, will be run in each laboratory with each extraction set. The five points shall span the linear range of the method. Suggested working standards for 1,3-dichloropropene range from 0.05 to 10 ng/ul. Suggested working standards for chloropicrin range from 0.005 to 0.6 ng/ul. Suggested working standards for MITC range from 0.025 to 10 ng/uL, and for methyl bromide from 0.05 to 6.0 ng/uL.

New stock solutions and working standards will be generated at least every six months.

Continuing quality control samples will be run with each extraction set and will include at a minimum, two spikes (one near the low range and one near the high range of the calibration curve) and one blank. Matrix spikes will be performed in both the primary and confirmation laboratories using the same procedure (i.e. spikes will be made directly into the sorbent tubes and then extracted). Matrix spikes will be performed twice per fumigation event in the primary laboratory and twice per extraction set in the confirmation laboratory. In addition, the primary laboratory will also use solvent spikes with each extraction set. Two injections (duplicates) per extract will be performed. Duplicate injections on all extracts will be performed one right after the other. Duplicate injections should have a minimum precision of 15%. If greater than 15% the chemist needs to determine the reason for this result, note the problem in the laboratory notebook, and then once corrected, run a third injection to confirm the problem was rectified.

The primary laboratory will not confirm positive samples unless the acute screening level is equaled or exceeded. Mass spectroscopy is the preferred method for confirmation of such concentrations. In addition, the confirmation laboratory was established to confirm 10% of all samples collected. Where mass spectroscopy is used, intra-laboratory confirmation will not be required since this is a definitive method.

Control charts will be maintained in the laboratory for comparison with continuing quality control spikes to verify the accuracy and precision of the method. With the exception of the CDFA confirmation laboratory, a running mean plus and minus one standard deviation will provide a warning limit. Two standard deviations around the mean is the control limit. One spike outside the warning limit will require an examination by the chemist for potential problems with equipment, extraction procedures, analytical procedures and/or calculations. Two sequential spikes outside the warning limit will require the chemist to cease work until the problem is corrected. One quality control spike outside the control limit will cease all analytical work until the problem is corrected. Methods for establishing and using control charts in the CDFA laboratory are described in Appendix U. Samples run with extraction sets having quality control spikes outside control limits will either be re-analyzed once the problem is corrected or adjusted based on detection of a systematic error. The course of action will be discussed with the study director at DPR.

Spikes and blanks returned to the laboratory from the field will be blind, i.e. analyte content will be unknown. Spikes and blanks will arrive with field samples, look like field samples, and their content will be unknown to the chemist.

The following describes spikes and blanks to be generated per fumigation event for sorbent tubes. Four trip spikes will be prepared for each fumigation, two at an expected low concentration and two at an expected high concentration. One low and one high will go to the primary laboratory. One low and one high will go to the confirmation laboratory. (In the case of a methyl bromide application, four trip spikes for chloropicrin will also be generated in the same manner outlined above.) Trip spikes will remain on dry ice and accompany all field samples (from one fumigation event) back to the laboratories. Trip spikes for the appropriate fumigant(s) will be generated when the 24-hour notice of application is received at the laboratory. Trip spikes shall be sent overnight mail, on dry ice, to the field sampling staff address provided. Once received by field staff, the ends of the tubes will be broken, caps replaced, security seals applied, and all appropriate paper work and sample storage conditions met as described above in section 4. Trip spikes must be kept on dry ice as field staff continue with sample collection. In addition to trip spikes, two fortified (sample) spikes will be generated by the primary laboratory and mailed with the trip spikes. A fortified spike is a spike that is mounted on an air sampler and run for on an air sampler just like a field sample. The schedule for fortified spike sampling is located in Appendix F. The two fortified spikes will be spiked at a high concentration. The Supervising chemist at the primary laboratory and the study director from DPR will agree on spike levels prior to study commencement.

In addition, to spikes, three blanks will be prepared per fumigation event. One sample blank where the ends of the tubes are broken, the tube is capped and sealed with the security seal, and left out at a sampling site. One sample blank will have the ends of the tubes broken, the tube capped and security seals applied. This sample will be placed on dry ice with the field samples. One blank stays in the laboratory to be analyzed when the field samples are returned to the laboratory.

A similar scheme will be conducted for canister spikes and blanks, if enough canisters are available. Currently, there are only 10 canisters and the sampling schedule for those canisters is in Appendix F. Members of the TAG decided upon the sampling schedule for 10 canisters at the Sept. 29, 1999 meeting. It is anticipated that sometime in November there will be 40 canisters available. Therefore, not all spikes and blanks described above will be possible. The final number of spikes and blanks will have to be negotiated between the primary laboratory, confirmation laboratory, US EPA, and DPR staff.

All data reported shall go through formal review in the laboratory prior to submission to DPR. Signatures of the supervising chemist and analytical chemist(s) will verify that this formal review has occurred.

6.5 Laboratory Reporting

The laboratory reports shall include the following information:

- Analytical results for all samples, trip spikes, fortified spikes, field blanks in ug/sample. Dates of extraction and analysis will be recorded for each sample.

- Total 1,3-dichloropropene will be reported (not individual isomers).
- Desorption efficiency data (individual results, i.e. not the mean) will be reported from each laboratory analyzing sorbent tubes.
- Mass spectroscopy confirmation will be reported, if performed.
- Case narrative (discussion of analysis and any problems encountered).
- Chain of Custody
- Sample receipt (Log-in) Forms
- Blank sample and blank continuing quality control results
- Matrix spike results and identification of corresponding samples in the same extraction set
- Solvent spike results (if applicable) and identification of corresponding samples in the same extraction set
- Control chart warning and control limits

7. DATA ANALYSIS

7.1 Calculation of Air Concentrations

Air concentrations will be calculated from the weight of analyte per sample (determined in the chemical analysis) divided by the volume of air drawn through an air sampler during the corresponding sampling period. Concentrations will be reported in ug/m^3 and also converted to parts per billion. Samples below the limit of detection will be treated as having one-half the detection limit.

7.2 Estimate Total Error

Sampling design error – The principal sources of sampling design error will be spatial and temporal variability, due to application and weather characteristics. Analysis of variance will be used to estimate the separate variance components due to Sites, Applications and Days. This will provide information on whether the allocation of samples between Sites, Applications and Days was effective.

Measurement error – Measurement error will be assessed by the following methods.

Data	Analysis	Type of error
Pairs of collocated samplers	Regression to estimate error of prediction	Total measurement error
Calibration curves run with each extraction set	Comparison of slopes and intercepts	Calibration drift
Matrix spikes analyzed with each extraction set	Estimate variance of recovery	Analytical variability
Matrix blanks analyzed with each extraction set	Estimate variance of blank	Analytical method background noise

7.3 Statistical Evaluation

The null hypothesis is that the maximum 24-hr concentration is greater than or equal to the acute screening level of 66 $\mu g/m^3$ (for MITC). The null hypothesis will be rejected at the (approximately) α=0.05 level if the maximum 24-hr concentration observed for the fumigant is less than 1/10 the screening level.

7.4 Air Concentrations, Weather, and Pesticide Use

Overlay maps showing the location of fumigant applications and general wind patterns will be used to aid in the interpretation of measured air concentrations.

The completeness of all data collected will be reviewed. An indication of data completeness will be provided in a final report.

The accuracy and precision of all data collected will be verified as indicated in the document above. Duplicate samples, trip spikes and blanks collected will be used to assess accuracy and precision.

REFERENCES

Ames, R.G. and J.A. Wisniewski. 1999. Hospital Discharges in Lompoc, California: An Analysis of Additional Data; Addendum to the Report: Illness Indicators in Lompoc, California. State of California. Office of Environmental Health Hazard Assessment.

Baker, L.W., D.L. Fitzell, J.N. Seiber, T.R. Parker, T. Shibamoto, M.W. Poore, K.E. Longley, R.P. Tomlin, R. Propper, and D.W. Duncan. 1996. Ambient air concentrations of pesticides in California. Environ. Sci. Technol. 30:1365-1368.

Beard K.K. 1994. An Evaluation of 1,3-Dichloropropene Air Concentrations Associated with Telone II Soil Fumigation in the Salinas Valley of California. DowElanco, Study ID DECO-HEH2.1-1-182(132).

Biermann, H. W. and T. Barry. 1999. Evaluation of charcoal tube and SUMMA canister recoveries for methyl bromide air sampling. Report EH 99-02. State of California. Department of Pesticide Regulation.

Burnett and Tambling, 1986.

Carter, W.P., Luo, C., Malkina, I.L. (1997) Investigation of the atmospheric reactions of chloropicrin. Atmosph. Environ. 31: 1425-1439.

DPR. 1995. Pesticide Use Reporting: An Overview of California's Unique Full Reporting System. State of California. Department of Pesticide Regulation

DPR. 1996. Pesticide Use Report. State of California. Department of Pesticide Regulation.

DPR. 1997a. Pesticide Use Report. State of California. Department of Pesticide

Regulation.

DPR. 1997b. Inspection Procedures. February 26, 1997. State of California. Department of Pesticide Regulation, Pesticide Enforcement Branch.

DPR. 1998. Pesticide Use Report. State of California. Department of Pesticide Regulation.

Fitzell, D. 1993. Ambient Air Monitoring in Contra Costa County during March 1993 after an Application of Metam Sodium to a Field. Air Resources Board, Engineering Evaluation Branch. Test Report C92-070A.

Gerstl et al., 1977;

Honaganahalli, P.S. and J.N. Seiber. 1997. Health and environmental concerns over the use of fumigants in agriculture: The case of methyl bromide. In: Fumigants Environmental Fate, Exposure, and Analysis. Editors: J.N. Seiber, J.A. Knuteson, J.E. Johnson, B.R. 1998. Analysis of Weather Patterns in Lompoc, California, Report EH 98-06. State of California. Department of Pesticide Regulation.

Keith, L.H. 1988. Principles of Environmental Sampling. American Chemical Society. 458 pp.

Leistra et al., 1974;
Leistra, 1974;

Majewski, M.S. and P.D. Capel. 1995. Pesticides in the Atmosphere. Distribution, Trends, and Governing Factors. Ann Arbor Press, Inc. Chelsea, MI. 214 pp.

Moilanen, K.W., D.G. Crosby, J.R. Humphrey, and J.W. Giles. 1978. Vapro phase photodecomposition of chloropicrin (Trichloronitromethane). Tetrahedron 34:3345-3349.

Ross, L.J., B. Johnson, K.D. Kim, and J. Hsu. 1996. Prediction of methyl bromide flux from area sources using the ISCST model. J. Environ. Qual. 25(4):885-891.

Seiber J.N., M.M McChesney, J.E. Woodrow, C. E. Mourer, T. S. Shibamoto. 1987. Pilot Analysis of Chloropicrin in Air. Air Resources Board, Contract A5-169-43.

Smelt et al., 1989.

Smelt and Leistra, 1974.

Turner and Corden, 1963

U.S. EPA. 1990. Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11. Code of Federal Regulations, Title 40, Part 136, Appendix B.

U.S. EPA. 1997. Compendium Method TO-15; Determination of volatile organic compounds (VOCs) in air collected in specially prepared-canisters and analyzed by gas chromatography/mass spectrometry (GC/MS); January 1997.

Wales, 1999;

Wilhelm, S.N., K. Shepler, L.J. Lawrence, and H. Lee. Environmental fate of chloropicrin. In: Fumigants Environmental Fate, Exposure, and Analysis. Editors: J.N. Seiber, J.A. Knuteson, J.E. Woodrow, M.V. Yates, and S.R. Yates. ACS Symposium Series 652. American Chemical Society, Washington D.C.

Wisniewski, J.A., R.G. Ames, R. Holtzer, M. Lipsett, and A. M. Fan. 1998. Illness Indicators in Lompoc, California: An Evaluation of Available Data. State of California. Office of Environmental Health Hazard Assessment.

Woodrow et al., 1983;

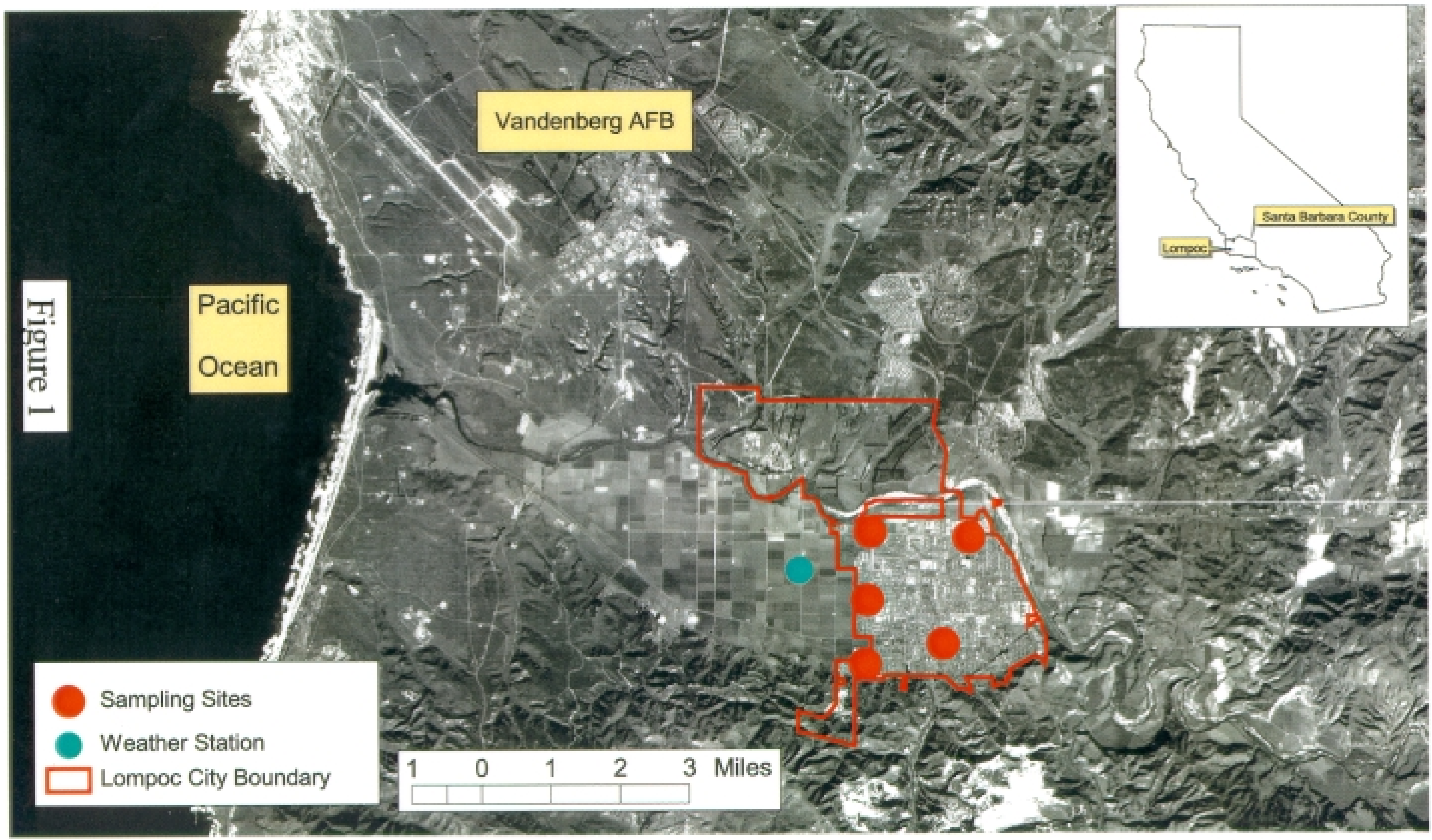
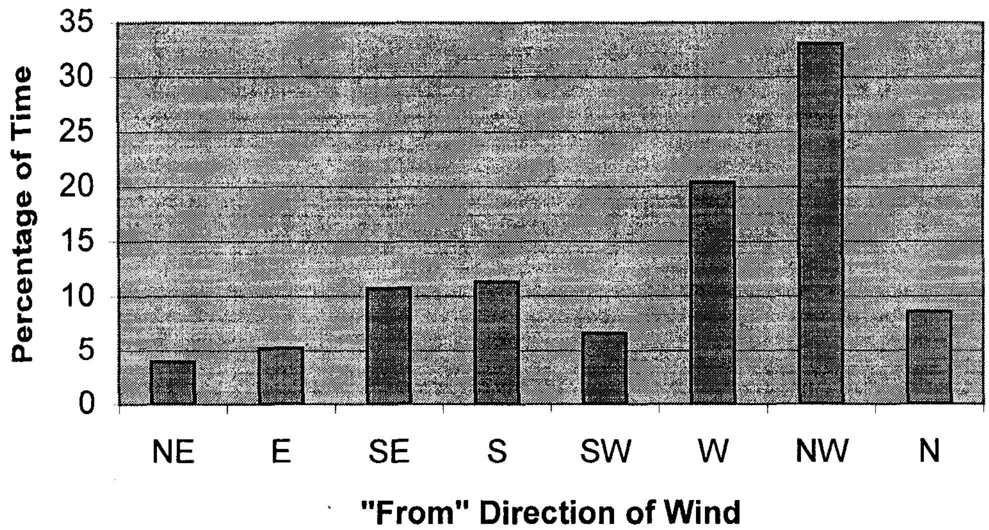

Vandenberg AFB
Pacific
Ocean
Santa Barbara County
Lompoc
Sampling Sites
Weather Station
Lompoc City Boundary
1 0 1 2 3 Miles

Figure 1

Figure 2. The percentage of time the wind blows from various directions during the months of November through January. Compiled from weather data collected during 1992-1995 at the H Street weather station located in downtown Lompoc.



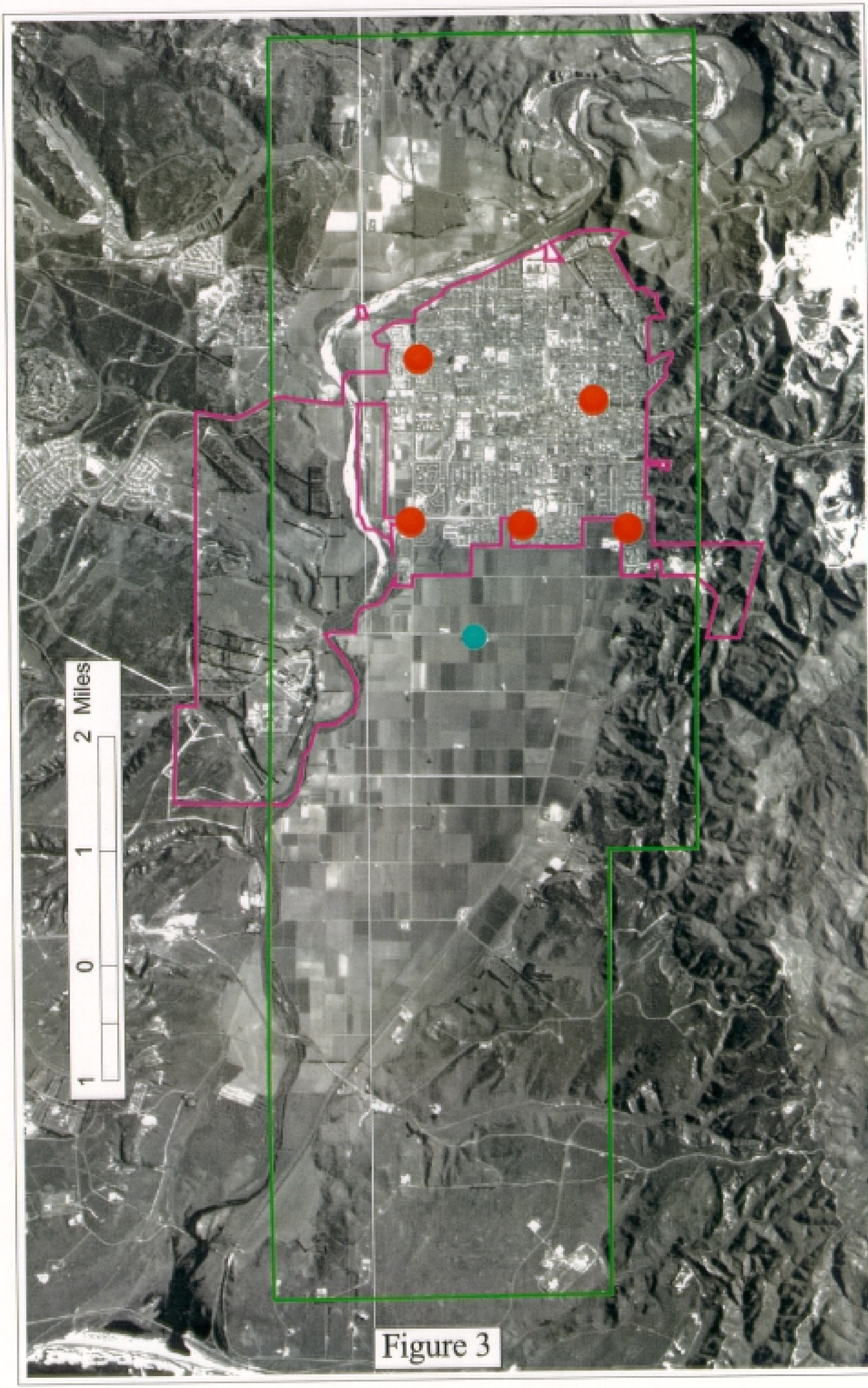


Figure 3

Fig. 4. Decision performance goal and error rate curve for the test of H_0: Maximum value >= 66 ug m^{-3} (n = 75).

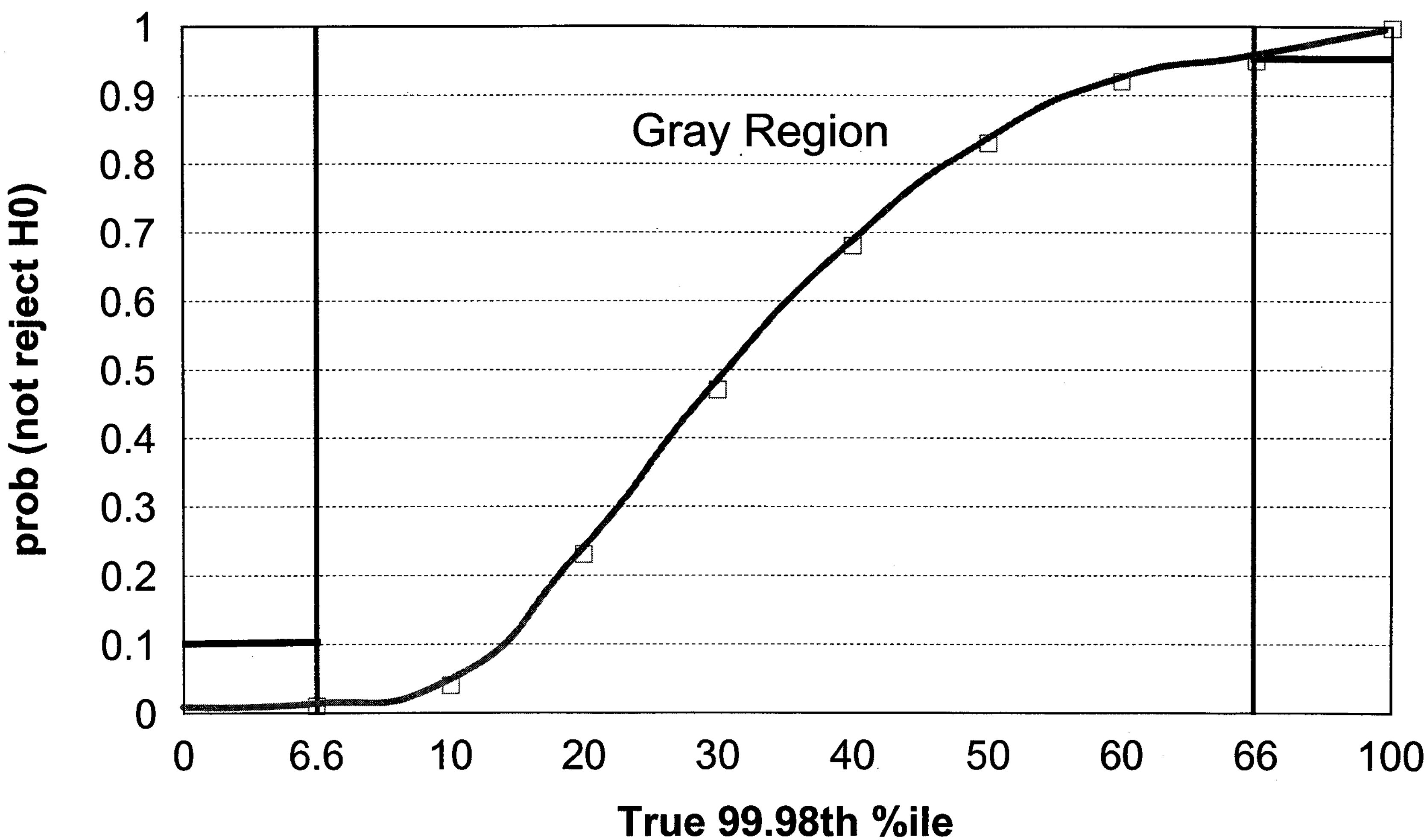


Table 1. Screening levels and recommended responses (decision rules).

Analyte	Exposure Scenario	Screening Level	Measured Level	Recommended Response
Methyl Bromide	**Acute,** 24-hour	820 ug/m^3	< 82 ug/m^3	Not a significant health concern. No immediate response. May still merit further analysis.
			82 - 820 ug/m^3	Not necessarily a health concern. Initiate a more refined analysis (revisit tox values, more exposure modeling, etc.).
			> 820 ug/m^3	Need to investigate and determine if interim mitigation measures are needed.
MITC	**Acute,** 24-hour	66 ug/m^3	< 6.6 ug/m^3	Not a significant health concern. No immediate response. May still merit further analysis.
			6.6 - 66 ug/m^3	Not necessarily a health concern. Initiate a more refined analysis (revisit tox values, more exposure modeling, etc.).
			> 66 ug/m^3	Need to investigate and determine if interim mitigation measures are needed.
Telone	**Acute,** 24-hour	140 ug/m^3	< 14 ug/m^3	No immediate response. May still merit further analysis.
			14 - 140 ug/m^3	Not necessarily a health concern. Initiate a more refined analysis (revisit tox values, more exposure modeling, etc.).
			> 140 ug/m^3	Need to investigate and determine if interim mitigation measures are needed.
Chloropicrin	**Acute,** 24-hour	29 ug/m^3	< 2.9 ug/m^3	No immediate response. May still merit further analysis, especially in light of the use of a 1 hour REL
			2.9 - 29 ug/m^3	Not necessarily a health concern. Initiate a more refined analysis (revisit tox values, more exposure modeling, etc.).
			> 29 ug/m^3	Need to investigate and determine if interim mitigation measures are needed.

Table 2. Top 30 Pesticides Used for Agricultural Production in the Lompoc Area (pounds).

Chemical	1996	1997	1998	Total
Metam-sodium	11251	34972	38660	84884
Fosetyl-aluminum	15841	14667	15211	45719
Maneb	10792	9028	8950	28770
Sulfur	7138	10194	8104	25435
Chlorthal-dimethyl	6804	6601	3427	16833
Iprodione	5052	4683	4460	14196
Chlorpyrifos	6040	4670	2847	13558
Glyphosate	1646	7227	2012	10885
Acephate	2921	2744	2293	7958
Propyzamide	2124	2587	2270	6981
Permethrin	3014	2161	1666	6841
Chlorothalonil	3654	1243	1805	6702
Dicloran	2292	2063	1877	6232
Methomyl	1963	3070	960	5993
1,3-dichloropropene	NRU	5850	NRU	5850
Simazine	4259	NRU	21	4280
PCNB	55	550	2793	3398
Thiodicarb	1395	1761	75	3231
Mancozeb	1231	997	999	3226
Vinclozolin	905	923	882	2710
Paraquat dichloride	226	2354	101	2681
Cryolite	1512	821	323	2656
Oxydemeton-methyl	729	1229	687	2645
Ethalfluralin	1849	381	385	2616
Bensulide	62	1425	1026	2513
Oxamyl	1188	749	556	2493
Alachlor	951	482	751	2184
Napropamide	812	208	1142	2162
Diazinon	525	909	700	2133
Malathion	1274	509	341	2124

NRU = no reported use

Table 3. Fumigants Used for Agricultural Production in the Lompoc Area, 1996 – 1998.

Chemical	Pounds	Acres	Applications	Year
1,3-dichloropropene	5850	19	1	97
Aluminum phosphide	3.2	NA[a]	2	96
Aluminum phosphide	7.9	NA	17	97
Aluminum phosphide	5.6	NA	16	98
Chloropicrin	91	7	3	97
Chloropicrin	2	1	1	96
Metam-sodium	38660	355	29	98
Metam-sodium	34972	489	33	97
Metam-sodium	11251	216	19	96
Methyl bromide	971	7	3	97
Methyl bromide	681	2	3	96
Total	92495	1096		

a. Not applicable. Aluminum phosphide is used primarily for commodity fumigation in closed or tarped containers or structures.

Table 4. Fumigants Used for Agricultural Production in the Lompoc Area by Month, 1996 – 1998 (pounds).

Month	Aluminum phosphide	1,3-dichloro propene	Chloropicrin	Metam Sodium	Methyl Bromide	Total
January	1.3		0	15960	208	16169.3
February	0.9	5850		108		5958.9
March	0.9		4	4621	883	5507.9
April	1.2			3951		3952.2
May	1.3			13482		13483.3
June	3.6			3873		3876.6
July	0.8		2	571	299	871.8
August	1.7			7197		7198.7
September	1.8			6938		6939.8
October	0.8		88	7440	263	7790.8
November	0.4			9525		9525.4
December	1.8			11218		11219.8
Total	16.5	5850	93	84884	1652	92495

Table 5. Summary of field sampling parameters and minimum chemical analytical parameters for the fumigants monitored in Lompoc November 1999 - January 2000.

Analyte	Sorbent Tube Adsorbent	Analytical Method	Extraction Solvent	Detector	Trapping Efficiency	Flow Rate (L/min)	Limit of Quantitation (ng/sample)	Limit of Quantitation ug/m3 8-hour	Limit of Quantitation ug/m3 16-hour
1,3-dichloropropene	coco. charcoal	OSHA/NIOSH	CS2/hexane	ECD	92%	3.0	150	0.10	0.05
chloropicrin	XAD resin	OSHA	hexane	ECD	87%	0.3	50	0.35	0.17
MITC	coco. charcoal	CDFA	CS2/hexane	NPD	94%	2.0	300	0.31	0.16
methyl bromide	pet. charcoal	CDFA	ethyl acetate	ECD	79%	0.015	200	28	14

Table 6. Township, range and sections used to define the agricultural boundary for the Lompoc air monitoring studies.[a]

Meridian	Township	Range	section		
S	06N	34W	1		
S	06N	34W	2		
S	06N	34W	3		
S	06N	34W	4		
S	06N	34W	5		
S	06N	34W	6		
S	06N	35W	1		
S	07N	34W	19		
S	07N	34W	20		
S	07N	34W	21		
S	07N	34W	22		
S	07N	34W	23		
S	07N	34W	24		
S	07N	34W	25		
S	07N	34W	26		
S	07N	34W	27		
S	07N	34W	28		
S	07N	34W	29		
S	07N	34W	30		
S	07N	34W	31		
S	07N	34W	32		
S	07N	34W	33		
S	07N	34W	34		
S	07N	34W	35		
S	07N	34W	36		
S	07N	35W	20		
S	07N	35W	21		
S	07N	35W	22		
S	07N	35W	23		
S	07N	35W	24		
S	07N	35W	25		
S	07N	35W	26		
S	07N	35W	27		
S	07N	35W	28		
S	07N	35W	29		
S	07N	35W	32		
S	07N	35W	33		
S	07N	35W	34		
S	07N	35W	35		
S	07N	35W	36		

a. See figure three for agricultural boundaries defined by the above Township-Range-sections.

Table 7. Some physical and chemical properties and break-down products of fumigants monitored in Lompoc during November 1999 through January 2000. All data are from the Department of Pesticide Regulation's Pesticide Chemistry Database, except where indicated.

Analyte	Molecular Weight	Solubility[a] in water (mg/L)	Vapor Pressure (mm Hg)	Hydrolysis Half-Life (days)	Aerobic Soil Half-Life (days)	Photolysis Half-Life (days)	Some Potential Atmospheric Contaminants Resulting from Degradation of the Analyte
1,3-dichloropropene	110.98	2250	29, 25 °C	11.3, pH 7, 20 °C	11.5 - 53.9	NA	
chloropicrin	164.4	2000	23.5, 25 °C	354, pH 7, 25 °C	0.4 - 5.1	1.3[c] to 20[d]	$COCl_2$ (phosgene) NOCl (nitrosyl chloride)e
MITC	73.12	8610	16, 25 °C	20.4, pH 7, 25 °C	0.5 - 50[b]	1.1[b]	CH3NC (methyl isocyanide) CH3NCO (methyl isocyanate)
methyl bromide	94.95	1380	1420, 20 °C	17, pH 8, 25 °C	1.5 - 20	NA	methane, bromide

NA = Not applicable. The UV absorption spectra for 1,3-dichloropropene and methyl bromide are below the shortest wavelenghts reaching the earth's surface (DowELANCO Study 63792, DPR Library Number 50046-33; Honaganahalli and Seiber, 1997).

a. 25 °C

b. Wales, 1999.

c. Wilhelm, et al. 1997.

d. Moilanen et al., 1978

e. These products have been measured under laboratory conditions or theorized (Moilanen, et al., 1978; Carter et al., 1997). Atmospheric measurement of these products were not found in the literature.